Summary #9

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Shock Initiation Characteristics of Ammonium Nitrate

A Summary report prepared for the
Department of Energy, Mines and Resources,
and other governmental contributing bodies

by

The Department of Mining Engineering
Queen's University
Kingston, Ontario

A. King
A. Bauer

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Table of Contents

		Page
Summary		1
Introduction		4
I	Shock Initiation Characteristics of Prilled Ammonium Nitrate	5
	Shock Initiation Characteristics of Molten Ammonium Nitrate	15
	Critical Shock Initiation Parameters for Molten Ammonium Nitrate	21
	Conclusions	25
II	Deflagration to Detonation Characteristics of Molten Ammonium Nitrate	26
	Summary	26
	Discussion	28
	Conclusion	36
III	Publications for Canadian Fertilizer Institute	38
IV	Appendix A	39

Summary

The object of the research conducted to-date was to determine under what conditions ammonium nitrate can be brought to a state of detonation by incidental and explosive derived shocks, especially under conditions of fire exposure.

Instrumented card gap tests on molten ammonium nitrate contained in 125 millimeter diameter Pyrex tubes, 400 millimeters in length, were conducted over a temperature range of 230°C to 260°C using Plexiglass attenuators. The explosive donor consists of ≈ 520 grams of C-4 plastic explosive assembled in a disc 120 millimeters in diameter and 30 millimeters in length. Shock velocities in Plexiglass attenuators of varying thicknesses were calibrated using a streak camera.

An equation of state for molten ammonium nitrate was developed at a temperature of 190°C, and a corresponding density of ≈ 1.42 grams/cm^3. This equation of state has been extended to much lower densities of ≈ 0.80 grams/cm^3, corresponding to temperatures approaching 260°C, at which point the molten ammonium nitrate is highly "aerated" as a result of thermal decomposition into N_2O and H_2O.

From the equation of state and card gap data, particle velocities in the molten ammonium nitrate were determined using an impedance mismatch technique. The critical impact pressures necessary to initiate molten ammonium nitrate to a state of

detonation at various temperatures were determined.

Critical booster weights, critical diameters (confined and unconfined), and velocities of detonation (as a function of temperature, confinement and charge diameter) were determined from 180°C to 260°C.

The bulk density of molten ammonium nitrate was determined from 170°C to 260°C. The sonic velocity in molten ammonium nitrate was determined over the same temperature range. By combining this data with ideal detonation state parameters of ammonium nitrate over a corresponding density range, the effect of aeration due to thermal decomposition products on the observed detonation process was determined.

The effects of charge density on critical booster weights were also investigated for the solid state over a density range of .76 to .92 grams/cm^3, in both cylindrical and hemispherical geometry. Centrally initiated hemispherical charges of ammonium nitrate prills (ρ_o < .82 gms/cm^3) with a mass of up to 1000 kilograms and a radius of 1 meter were successfully detonated and the process monitored with detonation velocity probes. Charges of comparable geometry using high density ammonium nitrate prills (ρ_o = .92 grams/cm^3) with a mass of up to 8000 kilograms and a radius of 2 meters were also successfully detonated.

The results indicate that the shock sensitivity of molten ammonium nitrate increases expotentially from 220°C to 260°C, at which point the shock sensitivity approaches that of nitroglycerine based dynamites.

High density ammonium nitrate prills (.85 grams/cm^3 ρ_o < .92 grams/cm^3) can be initiated and maintain a stable detonation provided the charge diameter is approximately 1 meter, and the critical booster weight is not less than ≈ 25 kilograms of TNT, or its equivalent.

Introduction

Ammonium nitrate is most commonly encountered in the chemical and fertilizer industries as either a prilled solid or a highly concentrated aqueous solution. Under certain conditions of fire exposure involving prilled ammonium nitrate, the molten state can be formed.

The shock sensitivity of the molten material at certain temperatures has been found by various workers to be much greater than that of the prilled or solid form commonly encountered in the chemical or fertilizer industries.

Assuming molten ammonium nitrate to be a prime mover in a sequence of events leading up to explosion of a bulk prill storage pile as a result of fire exposure, the explosion hazards then center around two factors: 1) the shock sensitivity and deflagration to detonation characteristics of the molten material, and; 2) the ability of large masses of prilled ammonium nitrate to initiate and detonate.

This paper presents results of tests designed to determine the shock initiation and detonation characteristics of the solid (prilled) and molten forms of ammonium nitrate.

The Shock Initiation Characteristics of Prilled Ammonium Nitrate

The rate of detonation and shock initiation characteristics of prilled or solid ammonium nitrate are strong functions of particle size, density (particle and bulk), confinement, primer weight and charge temperature. The effects of minimum primer size and critical diameter requirements were examined for ammonium nitrate prills of various densities in hemispherical configurations, which approximated bulk storage conditions. Hemispheres of 3 feet and 6 feet radii were constructed around a central priming core of 50/50 Pentolite or TNT (96 lbs maximum). Low and high density prills (i.e. $\rho_o \simeq 0.8$ gms/cm^3 respectively) were tested in the 3' radius hemisphere, or 1 ton size and high density prills were tested in the 6' radius hemisphere or 8 ton size. The results are summarized in Tables 1 and 2.

In relatively low energy yield explosives such as ammonium nitrate, where the heat of explosion is only 300 - 400 calories/gram, an adequate number of reaction centers become critical to detonation stability as the bulk density is raised. Even slight increases in bulk density from 0.8 to 0.9 grams/cm^3 dramatically increase both the critical diameter and minimum primer requirements.

In a detonation process, as for example, a detonating column of ammonium nitrate prills, the "grains" or prills burn

Table 1

2000 Lb. Hemisphere Test Data

Prill Type	Bulk Density(ρ_o) grams/cm^3	D*@ ρ_o (m/s)	D@ ρ_o (m/s)	N %
CIL LD	0.80	3400	3290	94
Genstar XP	0.74	3250	3200	97
Cyanamid LD	0.80	3400	3210	89
Cyanamid MD	0.86	3600	2670	55
Cyanamid HD	0.89	3740	F	-
Esso HD	0.91	3760	F	-
Western Co-op HD	0.90	3750	F	-

N is the fraction of the prills reacted inside the detonation head, and therefore able to supply energy for propagation of the detonation front.

Table 2

Velocity of Detonation of High Density
Ammonium Nitrate Prills

Trial No.	Primer Wt,Lbs	Bulk Density	D m/s	D* m/s	N %	Time to Consume Pile	Minimum Head Dimension
1	96	0.92 gm/cm^3	3460	3800	83	≈550μs	1 meter
2	66	"	2420	"	40	≈900μs	-
3	32	"	F	"	-	≈900μs	-
4	47	"	2140	"	32	≈900μs	-

In Trials 2 and 3 there were some unreacted prills around the perimeter of the crater in Trial #3.

In Trial #4 there were scattered prills in the vicinity, but not to the extent of that in Trial #3.

The crater from Trial #1 was the largest as shown in Table with the crater dimensions decreasing with the decreasing yield from each respective trial.

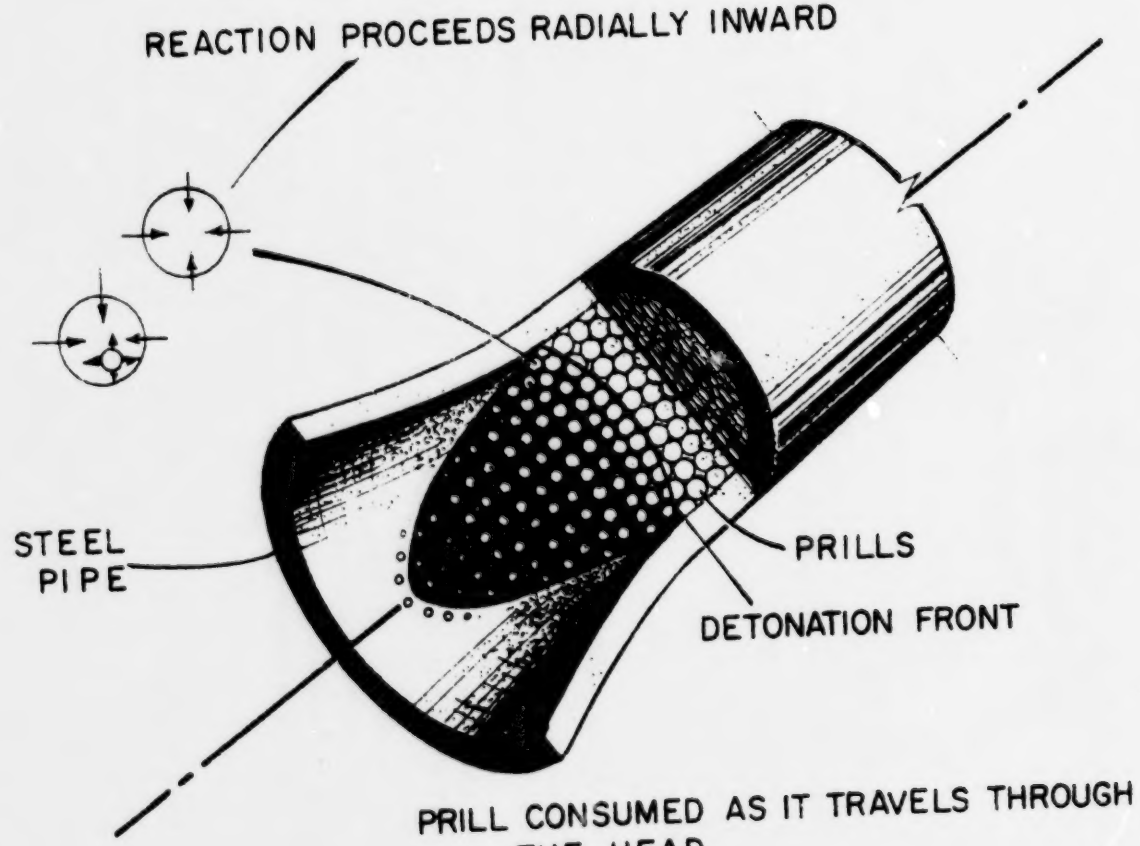

FIGURE 1: REACTION PROCESS FOR PRILLED EXPLOSIVES IN CYLINDRICAL GEOMETRY.

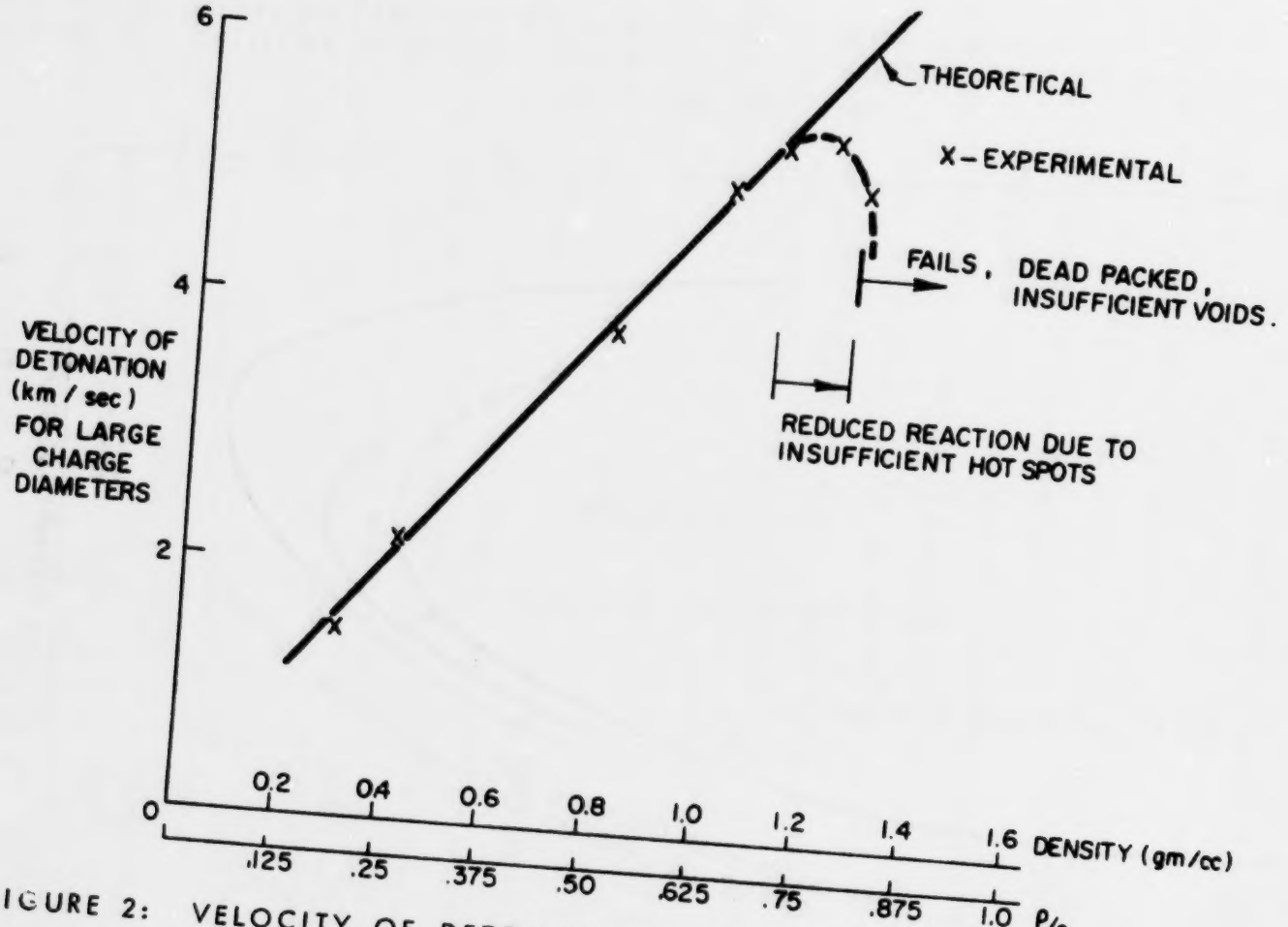

FIGURE 2: VELOCITY OF DETONATION FOR LARGE DIAMETER PRILLED AMMONIUM NITRATE/FUEL OIL CHARGES PLOTTED AS A FUNCTION OF CHARGE DENSITY.

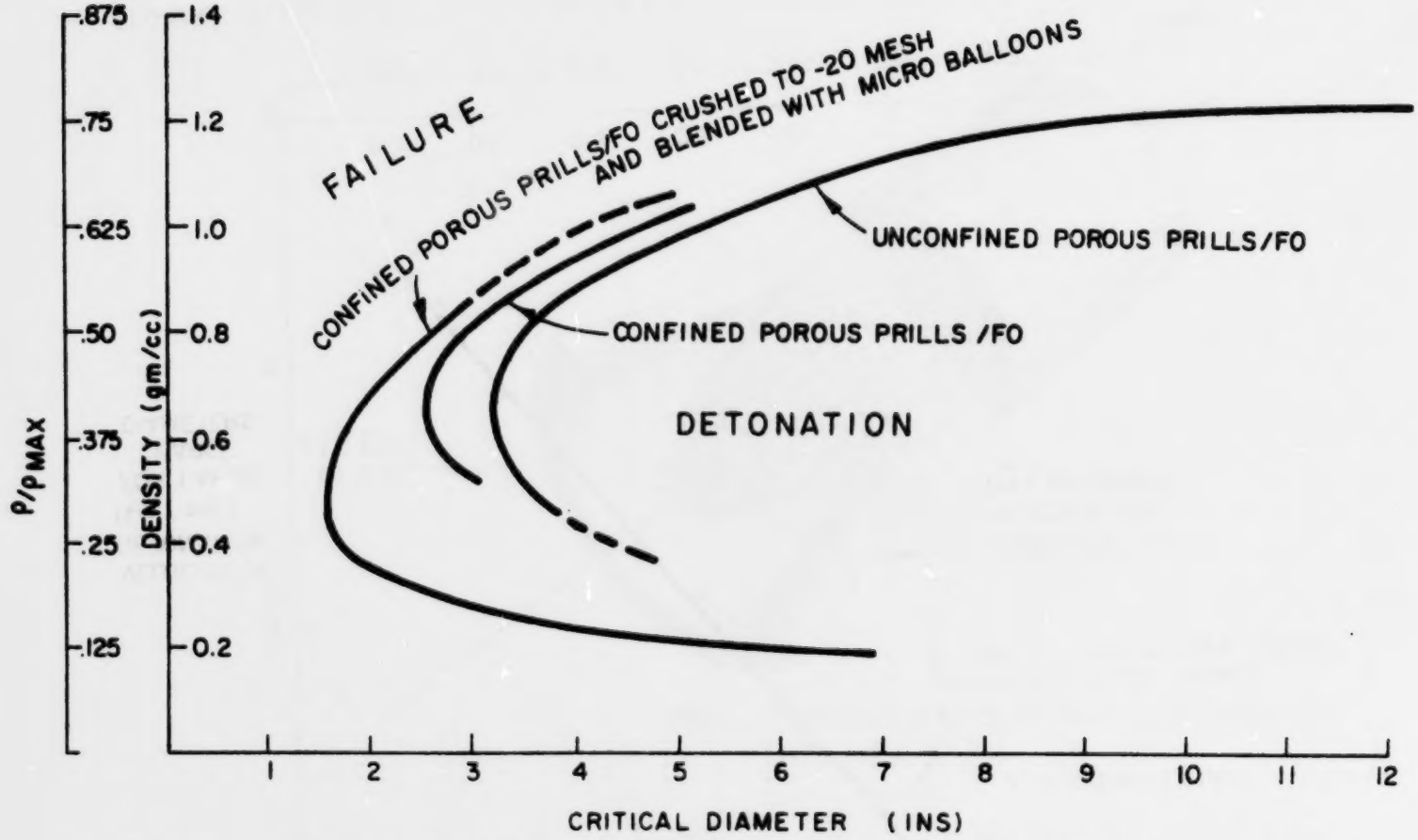

FIGURE 3: CRITICAL DIAMETER DEPENDENCE OF POROUS PRILLED AMMONIUM NITRATE/FUEL OIL MEXTURES ON CHARGE DENSITY.

from the outside inward. The burning process takes place inside a "detonation head", as shown in Figure 1. Only the energy released inside the detonation head can be used to propagate the detonation front. If all of the prills are consumed before leaving the detonation head, detonation is said to be ideal, and the velocity attained by the detonation front will be a maximum for that particular charge density.

In Figure 2, the effect of increased density upon the detonation velocity of ammonium nitrate/fuel oil mixtures (a typical "redox" explosive) in large diameters is shown. The dependence of redox explosive systems upon factors such as confinement and particle size is shown in Figure 3, which demonstrates the importance of providing a sufficient number of reaction centers. These centers, which in a solid explosive consist of air pockets, fissures or microfractures in the crystal structure, and annular spaces in or around the explosive grains become extremely hot when adiabatically compressed, yielding temperatures of several thousand degrees Kelvin. This results in a burning outward from these pockets or reaction centers which eventually coalesce to form a reaction front which provides energy to propagate a detonation wave.

If an insufficient number of "voids" or "pockets" are present in the explosive, the number of available reaction centers is reduced, thereby limiting the amount of energy available for propagating a reactive shock. Detonation failure can occur if

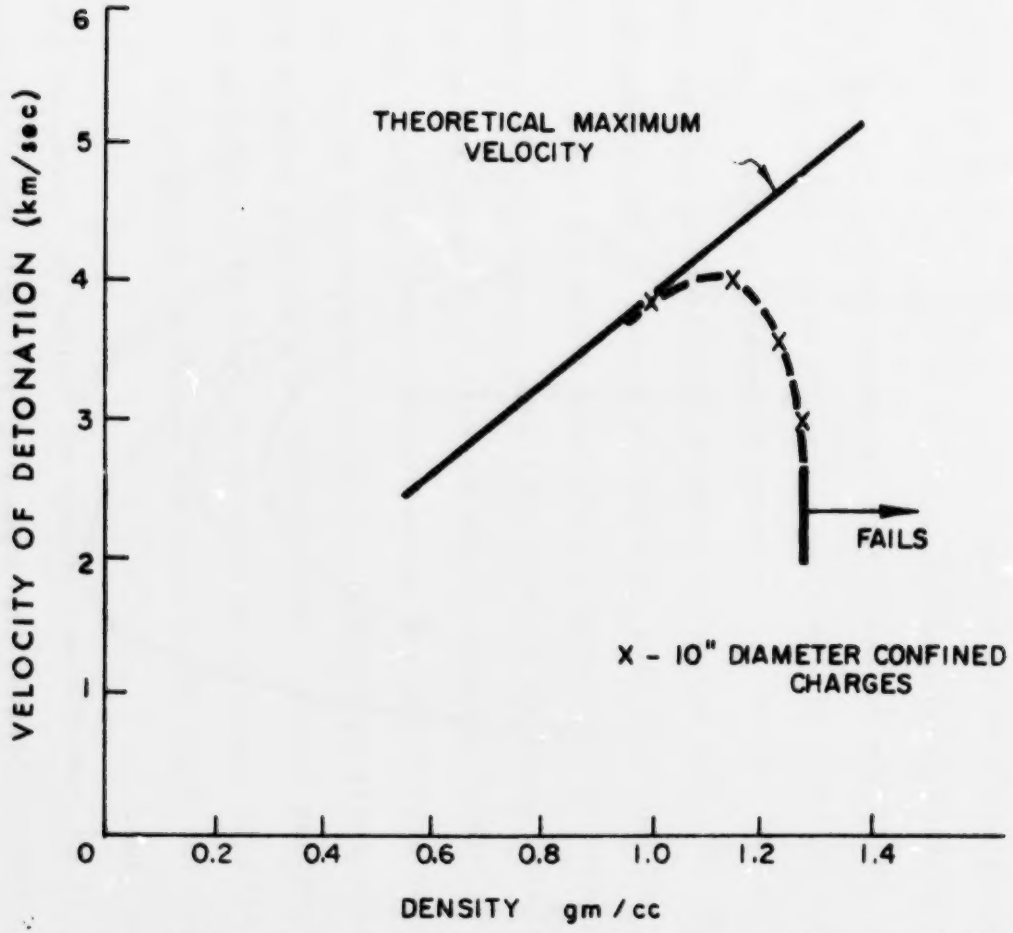

FIGURE 4: VELOCITY OF DETONATION FOR A 10 INCH CONFINED FUEL OIL/GAS BUBBLE SENSITIZED SLURRY PLOTTED AS A FUNCTION OF DENSITY.

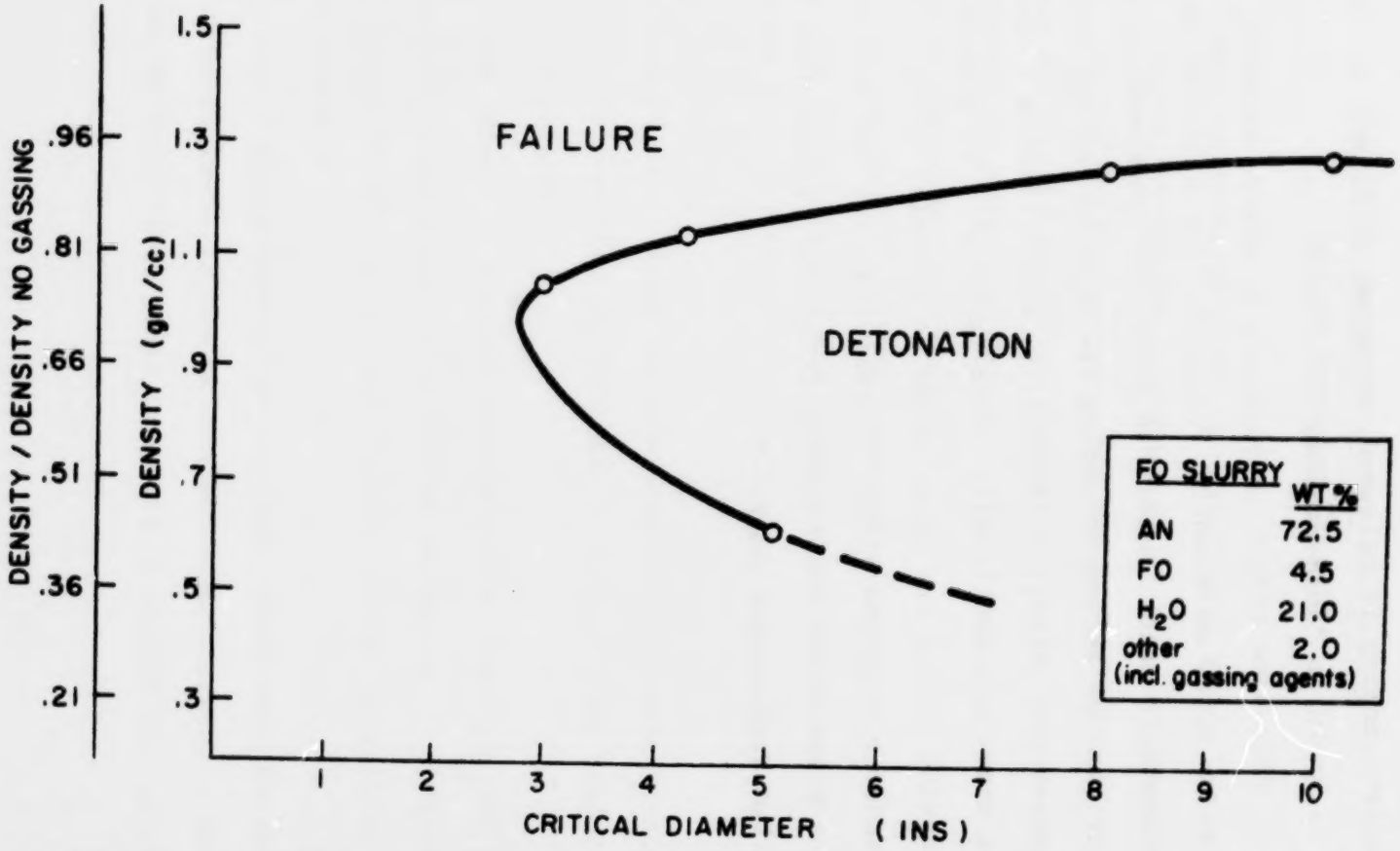

FIGURE 5: CRITICAL DIAMETER DEPENDENCE ON DENSITY FOR A FUEL OIL/ AMMONIUM NITRATE/WATER SLURRY AT 60° F.

insufficient energy is released, as shown in Figure 4. This effect is known as "dead-packing".

This same effect is apparent in slurry blasting explosives of the redox type, as shown in Figure 5. For slurries used under high hydrostatic heads, Bauer has shown that compression of explosive charges serves to reduce the size of the gas bubbles and increase the overall bulk density, which results in increased critical diameters and finally "dead-packing". To compensate for this, gassing agents are often added to slurries to introduce gas pockets or reactive sites, thereby bringing the bulk density down to a point where a detonation front can be sustained under the applied hydrostatic load.

The Shock Initiation Characteristics of Molten Ammonium Nitrate

When ammonium nitrate is heated well above its melting point of ≈ 170°C, it begins to decompose at a perceptable rate into N_2O, and dissociate into NH_3 and HNO_3. As the temperature approaches 260°C, gas evolution becomes very rapid, and the liquid appears to "boil" violently. This "aeration" lowers the bulk density, as shown in Figure 6.

In the case of molten ammonium nitrate, gas bubbles formed by the decomposition and dissociation reactions at elevated temperatures form the necessary reaction sites or "hot spots", as shown in Figure 7.

Liquid explosives can also exhibit the same "dead-packing" effects that are observed in some solid "redox" type explosives, as shown in Figure 8.

The effect of gaseous inclusions on lowering the bulk density as the temperature is raised is reflected in a decrease in the velocity of detonation and minimum primer weights as shown in Figures 9 and 10.

Once the pressure of an incident shock wave exceeds a certain critical level in the molten ammonium nitrate, a detonation process can be initiated. This pressure is called the critical impact pressure.

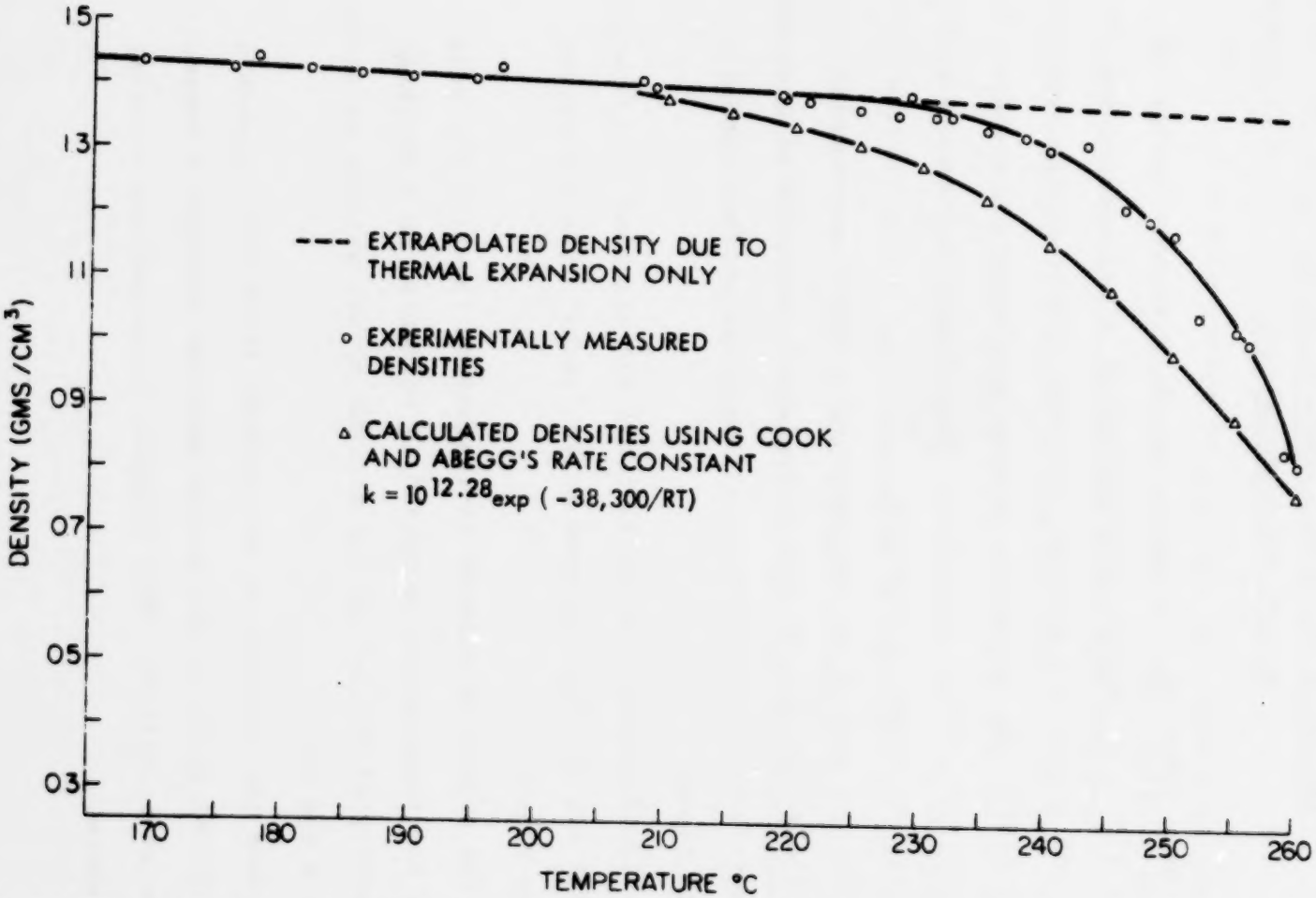

FIGURE 6: EXPERIMENTALLY DETERMINED DENSITIES AND CALCULATED DENSITIES FOR LIQUID PHASE AMMONIUM NITRATE FROM 170° C TO 260° C.

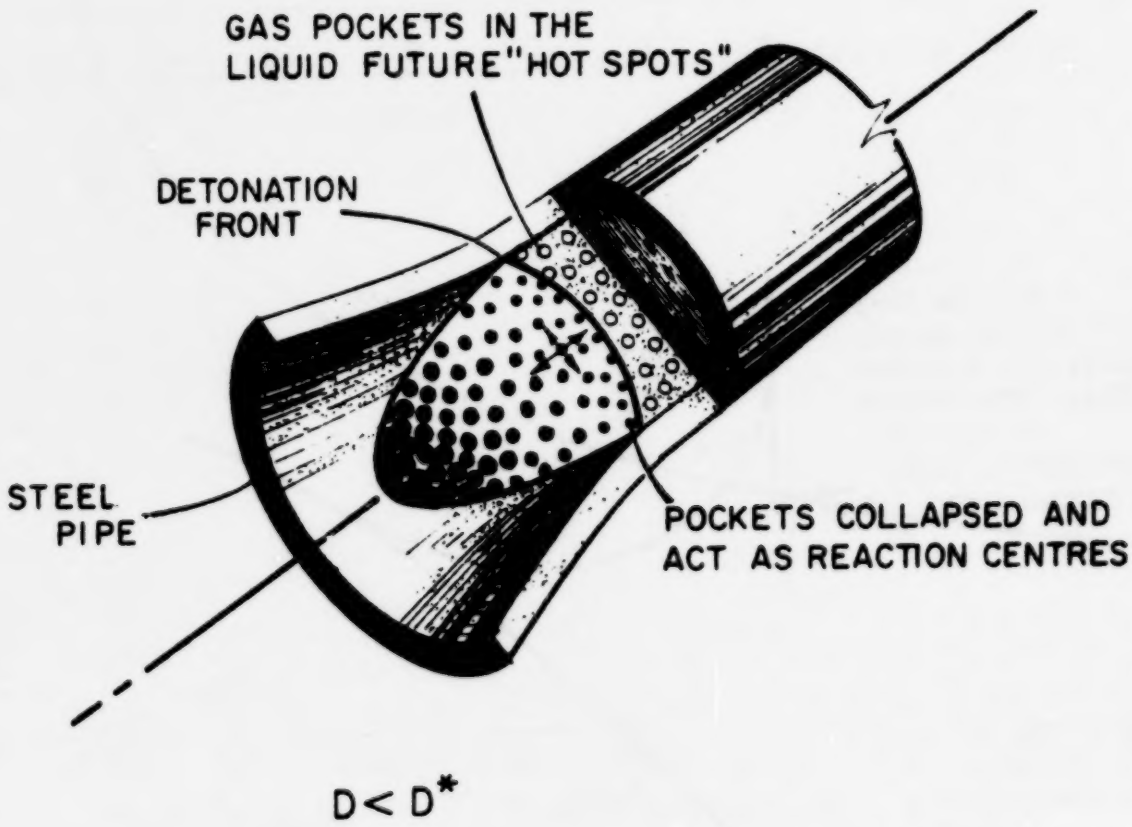

FIGURE 7: DETONATION PROCESS IN A LIQUID EXPLOSIVE ASSEMBLED IN CYLINDRICAL GEOMETRY.

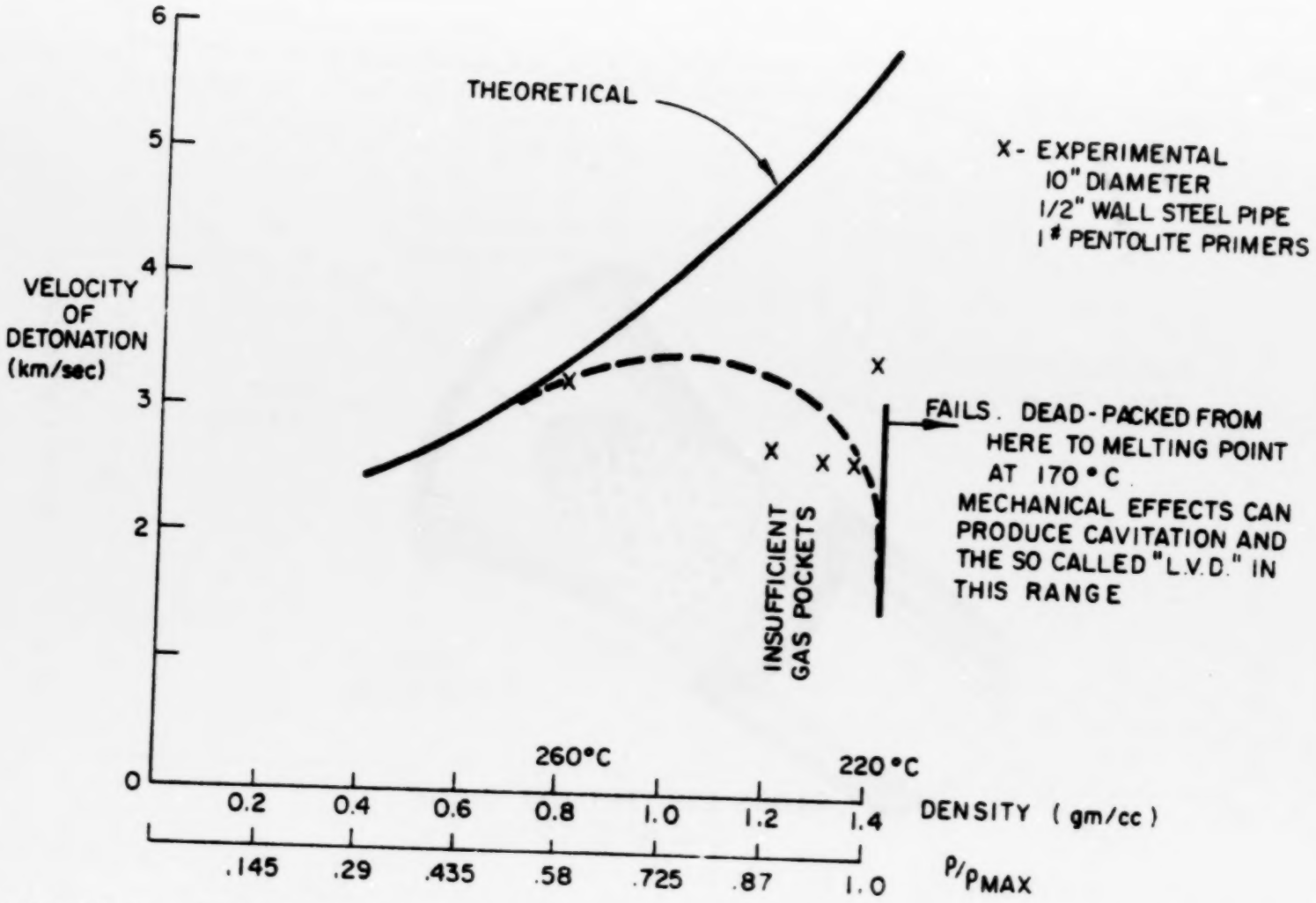

FIGURE 3: THEORETICAL AND MEASURED VALUES FOR THE DETONATION OF MOLTEN AMMONIUM NITRATE PLOTTED AS A FUNCTION OF DENSITY.

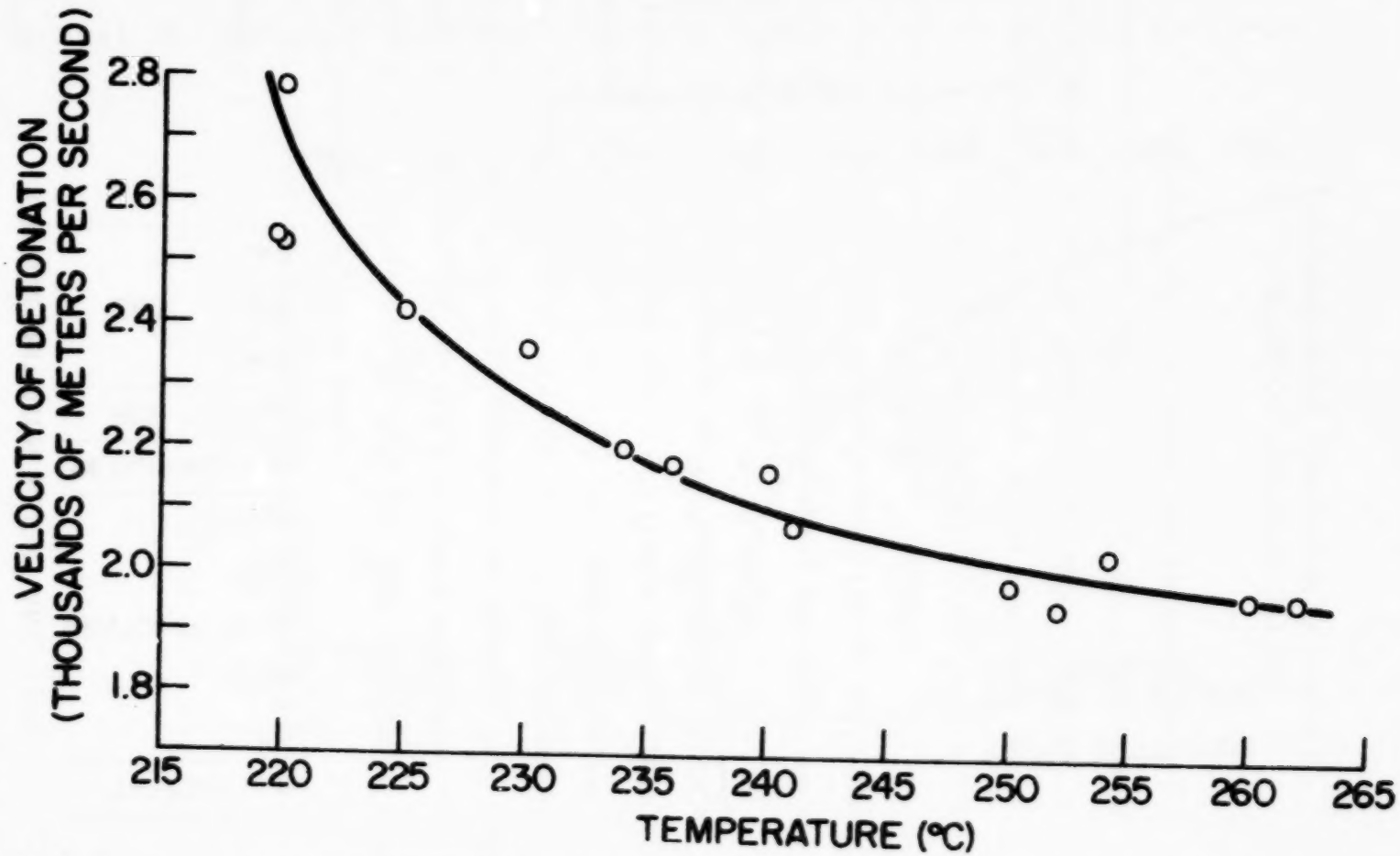

FIGURE 9: VELOCITY OF DETONATION OF MOLTEN AMMONIUM NITRATE AS A FUNCTION OF TEMPERATURE IN 5 INCH DIAMETER STEEL CANISTERS UNDER HEAVY CONFINEMENT (1/2" WALL).

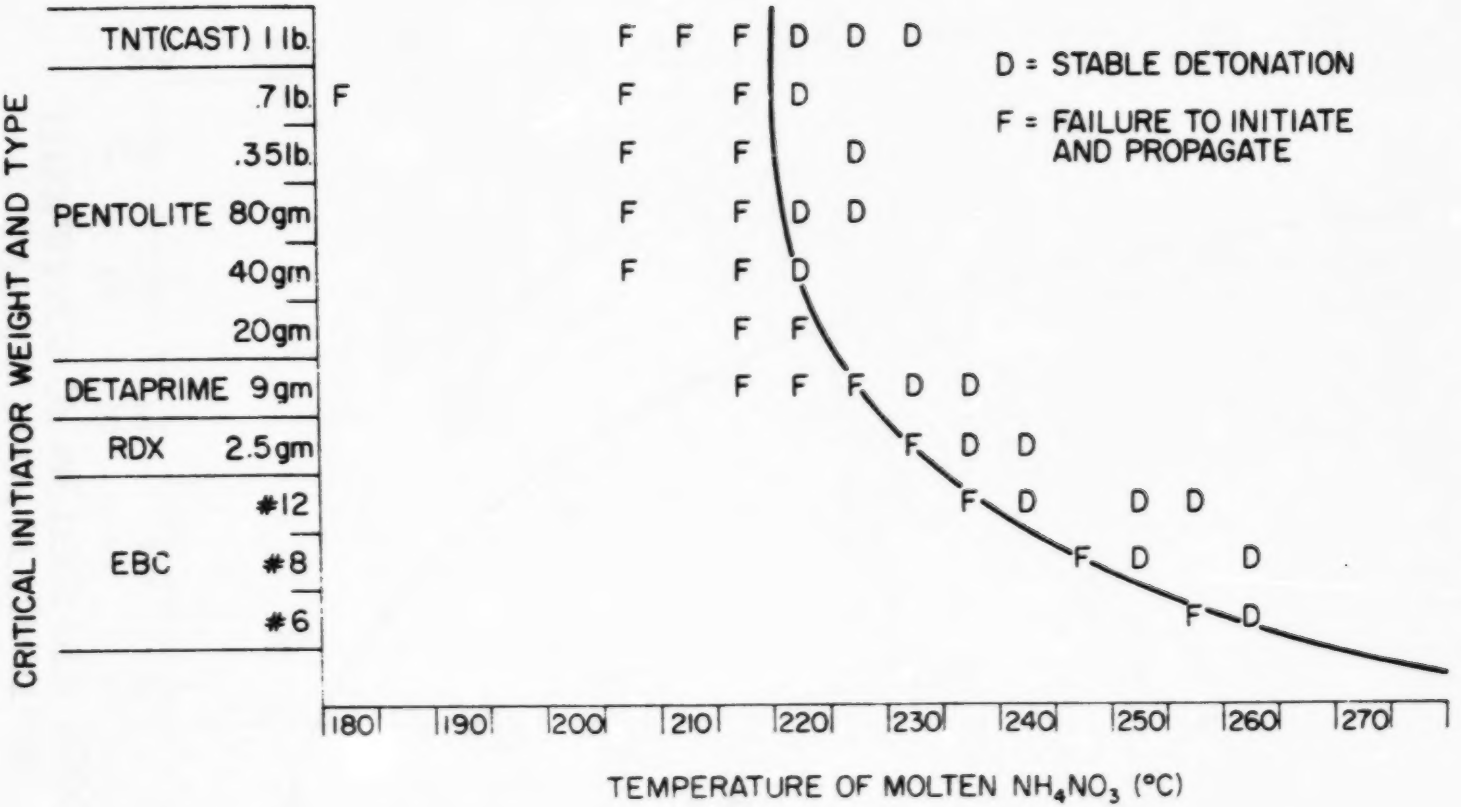

FIGURE 10: CRITICAL INITIATOR WEIGHTS AND TYPES FOR MOLTEN NH_4NO_3 AS A FUNCTION OF TEMPERATURE.

Critical Shock Initiation Parameters For Molten Ammonium Nitrate

Critical shock pressure and particle velocity were determined for molten ammonium nitrate as a function of temperature by means of an instrumented card gap test using Plexiglass as the shock attenuator and C-4 as the explosive donor.

Shock Hugoniots were developed for molten ammonium nitrate using streak photographic techniques. When these were used in conjunction with previously published shock Hugoniot data for Plexiglass, the critical shock initiation parameters were determined directly as shown in Figure 11.

A plot of critical primer weights and types as a function of temperature in molten ammonium nitrate results in a curve of remarkable similarity to that of the critical impact pressure plot, as shown in Figure 12, and the correlation between the two is evident. Tests in which hollow glass spheres were used in molten ammonium nitrate at 190°C to yield comparable densities normally occurring at 260°C, gave the same results as those for molten ammonium nitrate at 260°C.

The critical shock initiation parameters are summarized in Table 3.

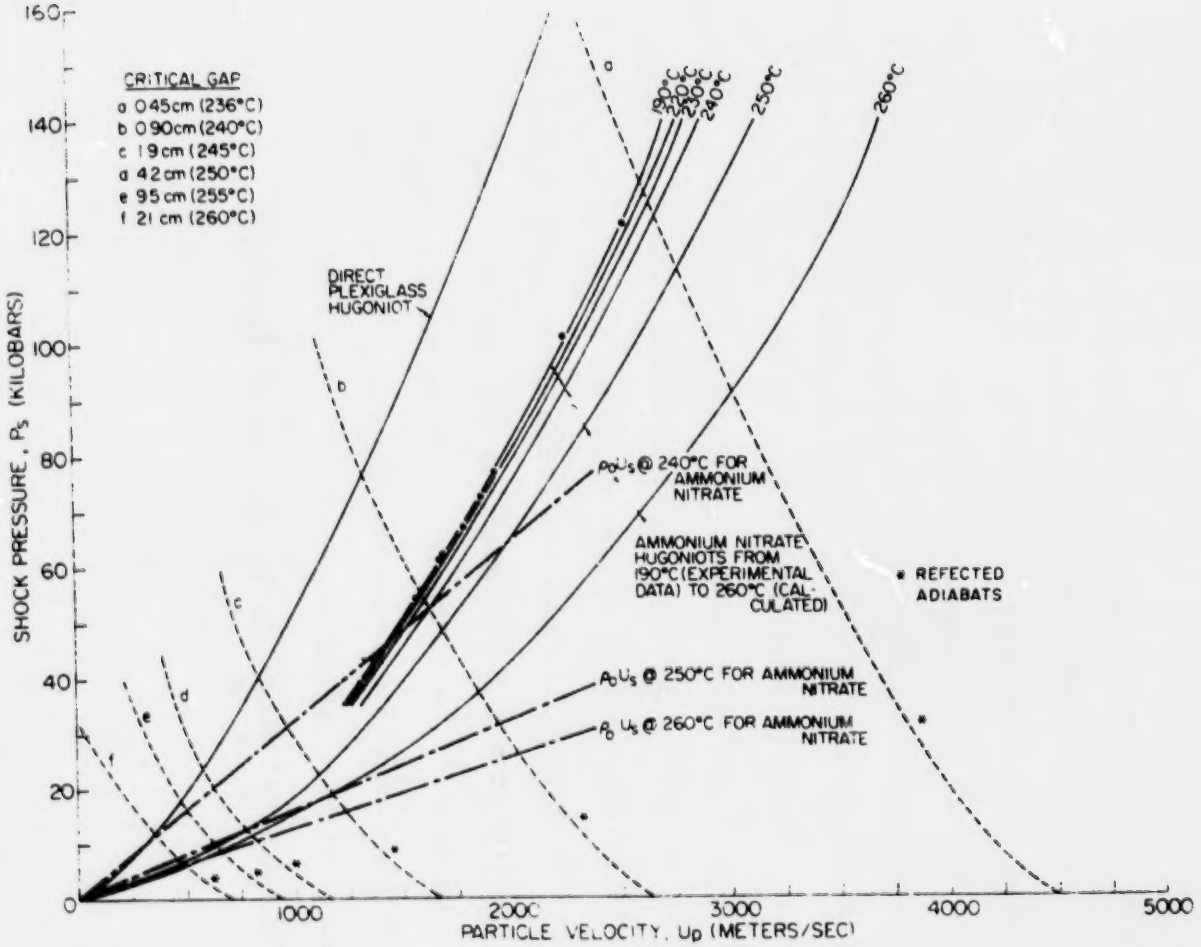

FIGURE 11: THE PRESSURE - PARTICLE VELOCITY HUGONIOTS FOR PLEXIGLASS AND MOLTEN AMMONIUM NITRATE ARE PLOTTED ON THE SAME PLANE. THE REFLECTED PLEXIGLASS ADIABATS INTERCEPT THE DIRECT HUGONIOTS FOR MOLTEN AMMONIUM NITRATE AT CRITICAL GAP.

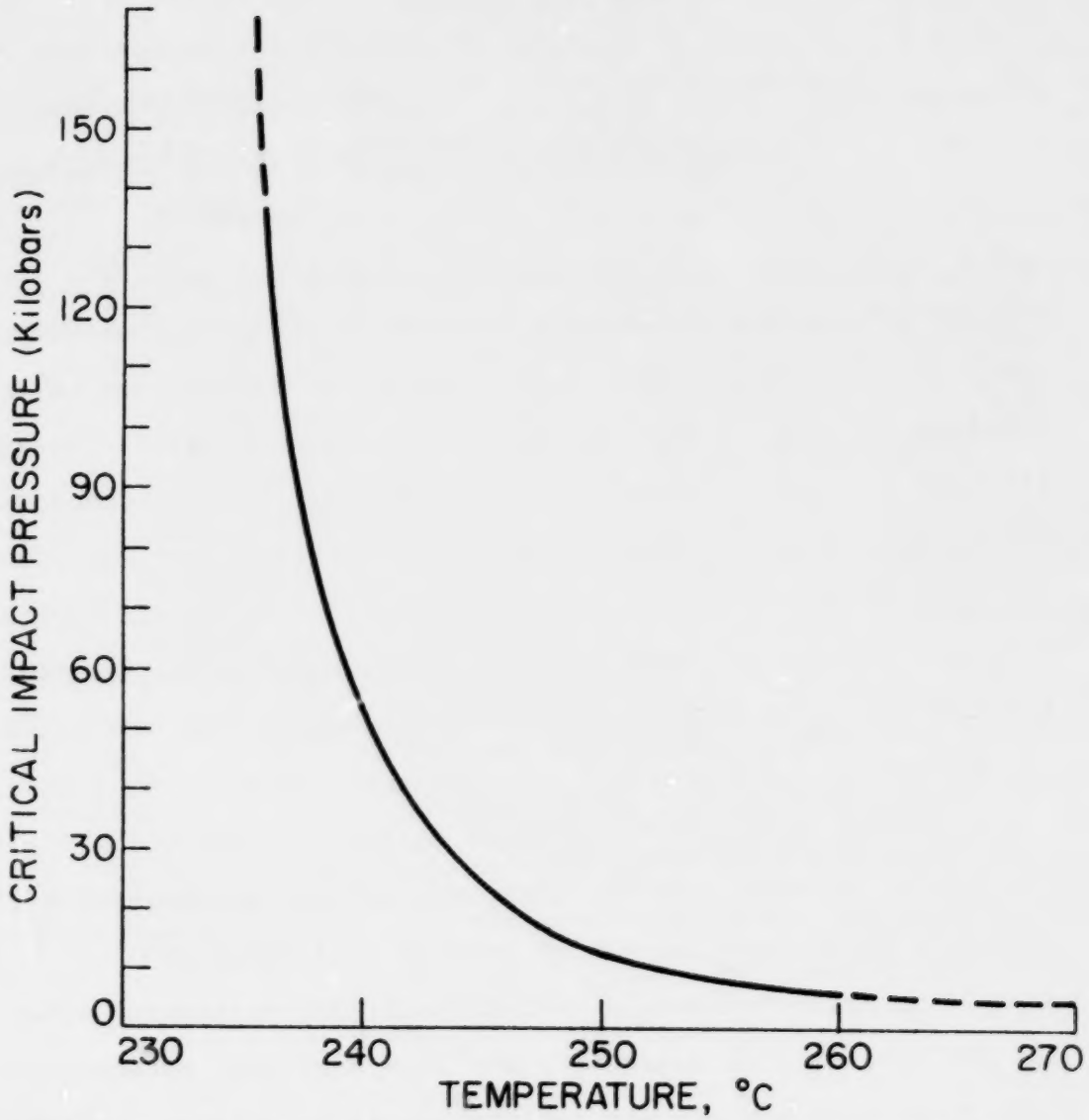

FIGURE 12: CRITICAL IMPACT PRESSURE FOR MOLTEN AMMONIUM NITRATE IS SHOWN AS A FUNCTION OF TEMPERATURE.

Table 3

Critical Shock Parameters for Molten Ammonium Nitrate

T°C	ρ_o Grams/ cm^3	Critical Gap, cm	Plexiglass Shock Velocity Meters/Second	Plexiglass Shock Pressure Kilobars	Ammonium Nitrate Critical Impact Pressure, KBars	Ammonium Nitrate Critical Particle Velocity Meters/ Second
230	1.37	.18	7250	>200	Off Scale	Off Scale
235	1.35	.45	6250	164	125	2645
240	1.32	.9	5000	76	52	1625
245	1.25	1.9	3950	34	24	1085
250	1.16	4.2	3500	24	13	775
255	1.05	9.5	3125	18	9.5	650
260	.8	21.0	2850	12	6.5	487
190	0.95 (Glass Bubbles)	>13 <15	>2950 <3000	≈15	≈ 8	≈ 550

Text and Conclusion

From card gap testing and a knowledge of the shock Hugoniots for molten ammonium nitrate, a critical impact pressure of approximately 6 Kilobars is required to initiate a stable detonation in molten ammonium nitrate at 260°C. This increases almost exponentially to ≈ 125 Kilobars at 230°C.

Increased shock sensitivity in molten ammonium nitrate as a result of temperature increase has been shown to be primarily a function of an almost similar exponential decrease in density as the temperature is raised. This is a direct result of aeration due to thermal decomposition products, and a rapid increase in the number of available hot spots.

The sensitivity of high density prills to explosive derived shocks as well as the ability of these prills to propagate a detonation in fixed diameters, has also been shown to be a strong function of density. The minimum primer weight for high density prills with a density of ≈ 0.9 grams/cm^3 is approximately 25-35 Kilograms of a TNT or Pentolite. The critical diameter is approximately 1 meter for prills of this density.

Clearly, high density prills can be made to sustain a stable detonation providing minimum primer and critical diameter requirements have been met, and this appears to be true for <u>all</u> forms of ammonium nitrate, provided the minimum void requirement has been met. Without this, no detonation is possible.

The Deflagration to Detonation Transition Characteristics of Molten Ammonium Nitrate

Report Summary

Rapid localized heating tests on small quantities (≈ 20 grams) of molten ammonium nitrate resulted in a mild explosion only when 2 or 3 grams of material remained in the vessel. The last measurable temperature was ≈ 340°C.

Burning gasoline and molten metals were dropped into molten ammonium nitrate at 260°C. Other than a slight elevation in temperature to ≈ 270 - 280°C, there was no reaction.

Various deflagrating or pyrotechnic compositions based on ammonium nitrate, such as mixtures containing Aℓ and carbon, Cu, Zn and other reactive metals were rapidly heated to study the deflagrating character of the mixes. Generally, the mixtures were very slow to burn at ambient temperatures when ignited on the surface, but often reacted explosively when the mixture was melted, especially in the presence of Cu.

Under confinement in metal pipes these mixtures reacted explosively when ignited, and this explosion was capable of detonating molten ammonium nitrate at 260°C under certain conditions.

4F Black Powder confined in metal pipes likewise initiated molten ammonium nitrate at 260°C.

4F Black Powder, contained in polyethylene bottles and ignited, was also capable of detonating molten ammonium nitrate at temperatures greater than 220°C, under the conditions tested.

Discussion

Burning gasoline and molten ammonium nitrate are quite immiscible and, due to the difference in densities between the two fluids, it is expected that the hydrocarbon would float on the surface of the molten ammonium nitrate. If a reaction was initiated, only a surface burning type of reaction would be expected to occur. Given the very small increase in temperature observed in the molten ammonium nitrate, it appears that the vaporization of the ammonium nitrate at the surface can accommodate any increase in temperature brought about by the oxidation of the hydrocarbon.

Molten lead and molten aluminum sink to the bottom of the vessel almost immediately, although some spattering of the molten metals was observed. Again, the ability of the molten ammonium nitrate to accommodate the influx of hot foreign objects depends primarily on the ability of ammonium nitrate to vaporize (dissociate into NH_3 and HNO_3). The slight rise in temperature which occurred serves to indicate that vaporization (or dissociation) may in fact have been instrumental in keeping the temperature of the bulk of the molten ammonium nitrate to only 270 - 280°C.

Even though aluminum and ammonium nitrate are capable of forming explosive mixtures, it appears that under the circumstances encountered here, any reaction, if it did occur, took place only at the surface of aluminum and probably ceased when

the aluminum solidified. The formation of an Al_2O_3 barrier on the Al surface may also have inhibited reaction at the interface.

The pyrotechnic or deflagrating type mixtures based on ammonium nitrate which were tested here do not appear to burn excessively fast when ignited at ambient pressures and temperatures. However, burning trials on a much larger scale of say 10 or 20 lbs, where ignition occurs over a much greater surface may behave quite differently. Generally, however, "cigar" burning with little noticeable flame was the preferred mode of decomposition for the compositions tested here, and large heat influxes were required to start the burning process.

At much higher temperatures, where the molten state was encountered, explosive reactions were a more frequent occurrence, especially in the presence of Cu and/or $Cu(NO_3)_2$.

In the presence of copper, formation of the tetrammine complex, $Cu(NH_3)_4(NO_3)_2$, is rapid when ammonium nitrate is in the molten state, and decomposed explosively on each occasion as it was strongly heated.

A study of the properties of "Tetramine Cupric Nitrate" was made by Picatinny Arsenal in 1943, where it deemed necessary to obtain information on the degree of hazard involved in the use of copper or copper alloys in equipment used for the manufacture of amatol. It was found that "Tetramine Cupric Nitrate" has approximately the same impact sensitivity as lead azide. It

Table 4

Rapid Heating Test Results for Ammonium Nitrate Mixtures Containing Organic and Metallic Constituents
50 Gram Samples

Test Number	Composition		Observations
1	AN	100%	Melting and accumulation of vapors above AN which turned red brown then exploded. AN ignited at edges and entire surface burned until AN consumed. No explosion.
2	AN Pb Powder	80% 20%	Melting and accelerated decomposition relative to Test # 1; Considerable foaming; No explosion.
3	AN Cr Powder	80% 20%	Accelerated decomposition even faster than Test #1 or #2; Considerable foaming; No explosion.
4	AN Cu	90% 10%	Accelerated decomposition relative to Test #1; Blue-green mass formed; Rapid propellant-like burning of residual towards end after AN reacted; Evaluation of considerable black smoke (CuO).
5	AN Zn	80% 20%	Violent deflagration after onset of melting. Considerable reaction. No explosion.
6	ANFO Zn	80.0% 20.0%	Violent deflagration after onset of melting. Considerable reaction and propellant like burning of residual mass.
7	ANFO	100%	Slight audible puffs and orange flashes after melting and ignition of vapors.
8	ANFO Cu Zn	77% 15% 8%	Rapid onset of deflagration of AN and Cu followed by ignition of residual mass. No explosion.

Test Number	Composition		Observations
10	AN	80%	Reaction similar to Trial #5 but not as violent. Most Al did not react. Much white smoke.
	$Cu(NO_3)_2$	10%	
	Al	5%	
	C	5%	
11	AN	100%	Decomposed normally with evolution of gases and white fumes until a temperature of ≈ 325°C was reached, at which point the residual mass estimated to be ≈ 1-2 grams exploded with an audible puff.
12	AN	99%	Same as Test #1; Slight explosion occurred at 330-340°C.
	Pb(Powder)	1%	
13	AN	95%	Same as Test # 1; Slight explosion at 323-330°C.
	Potassium Chloroplatinate	5%	
14	AN	95%	Same as Test #1 except mass turned blue-green when molten, then at 330-340°C, the residue exploded with a propellant - like "whoosh" with an orange flame and evolution of heavy black smoke (CuO).
	Cu	5%	
15	AN	95%	Same as Test #1.
	Pb(Powder)	5%	

Table 5

Rapid Heating Test Results for Ammonium [illegible] Containing Organic And Metal [illegible] 20 Gram Samples

Test Number	Composition		Observations
1	AN	85%	Very slowly decomposed
	Charcoal	15%	
2	AN	80%	Onset of reaction more rapid than in Trial #1; Burned at a faster rate than Trial #1.
	Charcoal	15%	
	$Cu(NO_3)_2$	3%	
	Cu	2%	
3	ANFO	100%	Slow to decompose; Considerable white smoke; some charring
4	ANFO	85%	Decomposed much like Trial #3 [illegible] at the end, when all the Al is either vaporized or otherwise reacted, the residue exploded with a brilliant flash
	$Cu(NO_3)_2$	10%	
	Al	5%	
5	AN	60%	Decomposed explosively with [illegible] brilliant flashes.
	$Cu(NO_3)_2$	23%	
	Charcoal	11%	
	Al	6%	
6	AN	85%	Slightly more exothermic than Trial #1, but not explosive. Considerable Al left unreacted.
	Charcoal	12%	
	Al	3%	
7	AN	85%	Quite exothermic with visible yellow flame - considerable white smoke. Al gave no evidence of reaction.
	Charcoal	13%	
	$Ni(NO_3)_2$	1%	
	Al	1%	
8	AN	85%	Same as Trial # 7.
	Charcoal	13%	
	$Cr(NO_3)_3$	1%	
	Al	1%	
9	AN	80%	Reaction similar to Trial #3 but not as violent. Most Al did not react. Much white smoke.
	Charcoal	15%	
	$Cu(NO_3)_2$	3%	
	Al	2%	

also resembles lead azide with respect to brisance, as determined from sand test data. In the explosion temperature test, Tetramine Cupric Nitrate exploded in 5 seconds at 331°C, compared to 335°C for lead azide. Friction and Ballistic Mortar tests were conducted on "Tetramine Cupric Nitrate" by Dr. A. King at the Canadian Explosive Research Laboratories (DEMR) near Ottawa in 1974. The friction test showed "Tetramine Cupric Nitrate" to lie somewhere between PETN and Perchlorate-Sulphur-Al mixtures in sensitivity. Ballistic Mortar tests showed that "Tetramine Cupric Nitrate" has 81% of the strength of TNT.

Clearly, the presence of (this metal complex) in a pool fire with molten ammonium nitrate represents a very hazardous situation.

From the test data presented in Table 4 it appears that aluminum becomes quite reactive in ammonium nitrate mixtures when $Cu(NO_3)_2$ is present, but otherwise remains relatively non-reactive.

Tests conducted with molten ammonium nitrate and powdered metals, as shown in Table 5 reveal Cu and Zn to be the most hazardous with respect to promoting violent exothermic reactions, with Zn being the most reactive and violent. When organic materials were present, these exothermic reactions proceed very rapidly, quite unlike the same compositions at ambient temperatures of approximately 20°C.

Confined ignition of deflagrating compositions of AN/C/Al by means of $Mg/Ba(NO_3)_2$ and/or Black Powder ignitors

generally resulted in a rapid burning of the composition and caused the end cap(s) of the confining pipe to be blown off.

The pipe itself, however, showed no visible signs of deformation, and the composition did not detonate, but merely deflagrated.

When these pipes were lowered into the molten ammonium nitrate at 260°C and the priming charge ignited, a probable detonation occurred in the molten ammonium nitrate only when ≈ 250 grams of mixture was used. When 80 grams of mixture was used there was a loud report but no violent explosion or detonation. They may indicate that the critical primer weight for a composition of this type lies somewhere between 80 and 250 grams under the conditions tested, but more tests would have to be done to confirm this.

When 80 grams of 4F Black Powder were placed a capped 1" diameter, 4" long schedule 40 pipe, and lowered into molten ammonium nitrate at 260°C as described above and ignited, the ammonium nitrate appeared to undergo a detonation.

Black Powder is capable of fragmenting these pipes rather violently, and the resultant explosion may be quite sufficient to impart a critical particle velocity in the molten ammonium nitrate of ≈ 500 meters/second.

By removing the confinement and relying mainly upon the heat flux and modest pressures developed by deflagrating 4F Black Powder, it was possible to initiate a strong explosion

(most likely a detonation) in molten ammonium nitrate at 270°C. This represents a drop in shock pressure of several orders of magnitude with respect to a #6 Electric Blasting Cap. It also represents a considerable increase in net energy, considering that ≈ 200 grams of 4F Black Powder was used. While this quantity is large, it was also possible to detonate molten ammonium nitrate at 230°C or 290°C with it.

The fact that molten ammonium nitrate at 284°C was not initiated with the 200 grams Black Powder priming charge indicates that more testing needs to be done in this area.

The observation at 270°C may be consistent with the proposed theory on DDT in molten ammonium nitrate however. (See Appendix I)

Conclusion

Surface burning reactions or deflagrations, appear to be ineffective in initiating a DDT in molten ammonium nitrate. If initiated over a large surface of several square feet, the results may be quite different. Similarly, if large amounts of molten metals were dropped into even larger quantities of molten ammonium nitrate, a different sequence of events may be observed. However, in the quantities and geometry tested here, a DDT appears unlikely.

The deflagration of ammonium nitrate-Cu compositions may present serious hazards from the point of view of being able to readily detonate, given the extreme sensitivity (comparable to lead azide) of the Tetramine Cupric Nitrate complex. This complex has been shown to form readily with molten ammonium nitrate, and more testing should be done on its ability to initiate a detonation in molten ammonium nitrate. The presence of this compound may represent the biggest single hazard in pool fires involving contaminated ammonium nitrate.

Cupric nitrate appears to be able to promote a rapid exothermic oxidation of metals such as Al which normally would not react too readily molten ammonium nitrate.

Zn is more readily oxidized than Cu and the presence of galvanized metal in and around fires involving ammonium

nitrate may be a source of potential hot spots.

Unconfined mixtures of ammonium nitrate with organic compounds such as charcoal, polyethylene, or paper can also serve as sources of potential hot spots in fires involving molten ammonium nitrate. When confined, these mixtures react explosively when ignited.

Exploding pipes containing deflagrating compositions such as ammonium nitrate/C/Al or 4F Black Powder appear to be capable of initiating a detonation in molten ammonium nitrate at certain temperatures and if present in sufficiently large quantities. The pressures represent a significant drop in that available from blasting caps or high explosive primers such as Detaprimes or Pentolite, although the total energy release is comparable or greater than some blasting caps or high explosive primers tested.

However, the ability of unconfined Black Powder to initiate a probable detonation in molten ammonium nitrate is very significant and more closely approximates the requirements of the proposed DDT theory previously described. Further testing in this area would be needed to evaluate fully a DDT mechanism.

PUBLICATIONS

FOR

CANADIAN FERTILIZER INSTITUTE

"A Review of Accidents with Ammonium Nitrate" (with A. King). Report for the Canadian Fertilizer Institute, June 1977, Contract No. OSU76-00262.

"A Critical Review of the EEC Detonability Test" (with A. King). Report for the Canadian Fertilizer Institute, June 1977, Contract No. OSU76-00262.

"A Critical Review of Thermal Decomposition Mechanisms of Ammonium Nitrate" (with A. King). Prepared for The Canadian Fertilizer Institute and Contributing Bodies.

"Priming Test Data for Assorted Canadian Ammonium Nitrate Prills" (with A. King, C.J. Preston, G. Dunn). Prepared for the Canadian Fertilizer Institute and Contributing Bodies, October 1977.

"The Detonation Properties of Liquid Phase Ammonium Nitrate" (with A. King, A. Bauer, R. Heater). July, 1978.

"The Detonation Properties of Ammonium Nitrate Prills," (with A. King, R. Heater). Prepared for the Canadian Fertilizer Institute and Contributing Bodies, November 1978.

"Critical Shock Initiation Parameters for Molten Ammonium Nitrate" (with A. King). Prepared for the Canadian Fertilizer Institute and Contributing Bodies, June 1979.

"The Deflagration to Detonation Transition Characteristics of Molten Ammonium Nitrate, Part I" NOvember 1979

APPENDIX I

A PROPOSED MECHANISM FOR THE DEFLAGRATION TO DETONATION TRANSITION OF MOLTEN AMMONIUM NITRATE

A Proposed Mechanism for the Deflagration to Detonation Transition of Molten Ammonium Nitrate

Molten ammonium nitrate is somewhat unique among explosive compounds in that its density (hence "porosity") can be varied by either raising or lowering the temperature in the fluid, especially at temperatures greater than 210°C. This property, more than anything else, is responsible for the great increase in shock sensitivity, especially at elevated temperatures approaching 260°C.

Price and Bernecker[†] observed in their studies of DDT in cast explosives that there is a critical interplay between the pore distribution of the charge (characterized by permeability) and the gas pressure in the ignition region for convective burning. If the gas pressure is too low, convective burning does not occur and the burning front is conductive (linear) flame front. This conductive flame front is characterized by a very slow but complete consumption of the explosive in layers, in this case, perpendicular to the axis of the tube. The rate of conductive (linear) burning is less than 10^{-4} mm/μs

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[†]Price, Donna, and Bernecker, Richard: Transition from Deflagration to Detonation in Granular Explosives. Naval Ordnance Laboratory, White Oak, Maryland, December, 1972.

in the explosives tested. However, above a certain critical gas pressure in the ignition region, pore combustion commences†. If the pressure in the ignition region is not maintained sufficiently long after the convective burning begins, the convective front may cease to exist unless adequately reinforced.

At 100% of the theoretical maximum density of the explosive, there is no porosity and the charge is impermeable. Hence, the ability of the explosive to undergo DDT will be determined by: a) a sufficiently rapid pressure rise in the ignition region caused by the generation of high product gas pressures; and b) the unburned explosive beyond the ignition region must be sufficiently sensitive to be initiated by a shock wave equal in amplitude to the high pressures generated near the ignitor.

The introduction of porosity into a charge does not mean that the charge will be permeable. The pores present may or may not be interconnected. If the pores are not connected, permeability is very low, and the criteria for DDT is essentially the same as discussed earlier.

As the porosity increases, the fraction of pores which are interconnected increases rapidly, although the permeability of the charge may still be quite low.

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†Price, Donna, and Bernecker, Richard: Transition from Deflagration to Detonation in Granular Explosives. Naval Ordnance Laboratory, White Oak, Maryland, December, 1972.

The formation of an ignition front in the pores of the explosive (convective burning) can now occur, and will depend upon the permeability of the charge, the adiabatic flame temperature of the explosive, the ability of the confinement to allow a critical "driving" pressure to be set up.

As more porosity is introduced into the charge, the gas flow can no longer be described as choked. Enough pores may be connected to permit flow which may be described as steady state. However, the time to produce a rapid acceleration in dP/dT is now longer than in earlier cases since more explosive must be burned to compensate for the energy flow (in the gas phase) out of the burning area.

In any study of detonation phenomena, an important quantity is the time to detonation relative to the initial application of stimulus. In the case of DDT's, this is the time from ignition of the explosive charge at the ignitor interface to the point at which detonation begins.

This time to detonation, t_D, increases as the permeability increases, and the position of onset of detonation also increases with increasing porosity.

For very permeable charges, the runup length to detonation increases with increasing porosity. However, the energy losses from the burning region near the ignitor can be so large as to prevent the attainment of a sufficiently large dP/dt to effect transition. For energy deficient explosives

such as ammonium picrate (and ammonium nitrate) pressure increases at these densities can be quite slow and non accelerating. The absence of an accelerating dP/dt does not mean the absence of a high pressure. Pressure may increase linearly to several kilobars but in the absence of a rapidly rising dP/dt, no compressive waves emanate from the burning region.

These observations by Price and Bernecker on DDT phenomena in cast shell fillers indicate how complex the DDT phenomena can be. The DDT process in an aerated, low energy fluid can be even more complex. When that fluid has a variable density-temperature relationship, and exhibits an increased reaction rate with temperature, the problem rapidly becomes even more complicated. This is the case with molten ammonium nitrate.

Assuming that the temperature-limiting mechanism for molten ammonium nitrate has been short circuited, either by extremely rapid overheating, or by confinement, or both, an uncontrolled temperature rise becomes possible.

This event must then be coupled to a forced convection of hot, gaseous, decomposition products throughout the as yet unreacted material.

Once this occurs the reaction rate and subsequent pressure and temperature rise can become accelerated. If the acceleration of the above quantities is sufficiently rapid, a shock wave may form, followed by a detonation of the bulk of the remainder.

Therefore, the following constraints are proposed which provide for the possibility of initiating a DDT in molten ammonium nitrate:

a) extremely rapid overheating (and/or confinement) of a quantity of molten ammonium nitrate in contact with a larger pool;

b) a geometry conducive to providing a flux of hot, gaseous, decomposition products through the unreacted material;

c) a critical depth of fluid which may be a function of charge temperature and confinement, as well as ignitor strength

d) a sufficiently hot (hence porous) charge of molten ammonium nitrate must be provided. This sets a minimum charge temperature of 220°C if DDT is to occur.

POOR

QUALITY

ORIGINAL